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" AN ELECTROLYTIC PROCESS FOR THE PRODUCTION OF ANODISED ALUMINIUM PLATES WITH A DESIRED PATTERN IN COLOUR "

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi - 110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention.

PRICE: TWO RUPEES

This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and VENKATARAMAN BALASUBRAMANIAN, Senior Scientific Assistant both of them are employed in Central Electrochemical Research Institute, Karaikudi-6, TamilNadu, India and are Indian Nationals.

This invention relates to improvements in or relating to preparation of labeles designs and photographs of permanent nature of anodised aluminium without silver by electrolytic pigmentation.

Hitherto it has been proposed to use methods such as Silk screen method and offset printing techniques on anodised aluminium for making lables and desings. Silver deposited inside the pores of anodised aluminium was also used for preparing Black and White photographs by adopting usual photographic technique.

There are some disadvantages in the above methods which are as follows:

Silk screen method can be used only for reproducing line compositions; fine lines and half-tones can not be reproduced with great precision. Silk screen and in offset methods the dye stuffs used for colouring are organic in nature which are not light fast and hence unsuitable for out door exposures. In the last method namely, the photographic method anodised aluminium is impregnated with photosensitive salts in the pores .....

of the oxide film and developing the image, involve costly chemicals such as silver salts.

The object of the present invention is to obviate the above disadvantages by using anodised aluminium (here the word aluminium includes alloys of aluminium also) for making labels, designs and photographs by Electrolytic pigmentation method using inorganic salt solution either using A.C. or D.C. current supply.

To these ends, the invention consist in anodising aluminium in 5 to 50% V/V sulphuric acid using direct or alternating current of 1.5 A 2.3 A/dm^2 at 20 ± 5°C for 20 to 40 minutes. Conventional acid resistant photo sensitive resist is uniformly coated over the anodised surface and dried in the dark. The sensitised anodised aluminium plate is exposed to any film positive (half tone or line) using ultra violet radiation for a period of 5-15 min. The exposed anodised plate is treated in conventional developed. In this process unhardened portion of the resist will be removed by the developer. After developing the image, it is fixed and electrolytically coloured in Nickel, copper, cobalt, Bismuth or Tin salt solution using copper, Nickel, graphite or carbon as counter electrode employing A.C. or Director Current. During electrolysis the image area is electrolytically coloured. The colour depends upon the metallic salt solution, period of treatment and conditions of electrolysis. The image then obtained is washed dried and the resist on the surface is removed with the solvent. The photograph, design or label thus obtained on anodised aluminium is sealed in boiling water for 20 - 30 minutes. The label, photograph or design thus obtained is elegant smooth and colour fast. The designs thus obtained are most suitable for outdoor architectural applications.

The following examples are given to illustrate the invention and not to limit the scope of the invention.

EXAMPLE-1

Mechanically polished degreased 20 Aluminium plate of size 3" X 4" with 1" handle was first alkali cleaned in 10% sodium

hydroxide for 2 minutes and washed in tap water and desmutted in 20% HNO_3 for 2 minutes. The aluminium plate thus cleaned is washed and rinsed with distilled water and jigged using aluminium jig. The plate is anodised in 10% V/V sulphuric acid electrolytic (sp-gr. 1.84) at 20 ±2°C for 30 minutes at 1.5 A/dm^2 current density. The anodised aluminium plate was washed and dried in the cold. Conventional acid resistant photo resist is applied on the surface uniformly using a coating device. The coated photo sensitive resist is dried cold in the dark. The sensitised anodised aluminium plate thus obtained is exposed to ultraviolet source through a photo positive for 10 minutes. The exposed plate was developed in trichloroethylene and washed in tap water and rinsed with distilled water. Now the plate is ready for electrolytic colouring. The anodised and sensitised plate is taken as one electrode and copper as the other electrode and electrolytically coloured using a current density of 0.4 A/dm^2 in an electrolyte containing 20 g/l copper sulphate with pH 1.5 adjusted with sulphuric acid. The plate was coloured for 5 minutes at 9 V to get copper red colour. The plate was washed fried and the photo resist was removed with trichloroethylene and sealed in boiling hot water for 30 minutes. The image obtained was very elegant, and faithful reproduction of the image was obtained.

EXAMPLE-2

8518 aluminium alloy plate was precleaned anodised and sensitised with photo resist as given in example 1 and exposed to photo positive and the image was developed. Then the sensitised Al alloy plate was electrolytically coloured in an electrolytic colouring solution containing 2 g/l bismuth oxide. 2 g/l gelatin and 10 g/l sulphuric acid. The anodised aluminium plate was held as cathode using a graphite anode in the above electrolyte and 0.5 A/dm^2 D.C. current was passed for 20 minutes to get grey colour. The coloured image was washed, dried and the photo resist was removed and sealed in boiling distilled water for 20 minutes. The image obtained was very sharp and clear.

EXAMPLE-3

268 aluminium alloy plate was precleaned, anodised and

sensitised with photo resist as in example 1. The sensitised anodised aluminium was exposed to half tone phto positive for 15 minutes and the image was developed using trichloroethylene. The plate was washed rinsed and elctrolytically coloured using A.C. in a Nickel bath, containing Nickel sulphate 100 g/l Boric Acid 50 g/l Ammonium sulphate 30 g/1 copper sulphate 10 g/l. The pH of the bath was 4 and nickel was used as counter electrode. A current density of 0.4 A/dm^2 was employed. After 10 minutes duration the image area was coloured brownish black. Later the photo resist on the non image area was removed and sealed in boiling hot water. The image obtained was sharp and uniform.

EXAMPLE-4

57S aluminium alloy was polished, precleaned as in example 1 and anodised in 20% V/V sulphuric acid at 20 ± 2°C for 40 minutes at 1.5 A/dm^2 current density. The anodised plate was coated with photo sensitive resist in the dark and dried well. The sensitised plate was exposed to ultra violet source through a positive transparency for 10 min. and the image developed. The developed palte was electrolytically coloured using A.C. in a bath containing Stannous sulphate (saturated) and 10 g/l sulphuric acid using graphite as counter electrode. The image area of the anodised plate coloured Black in 10 min. at 0.4 A/dm^2 current density. The coloured plate was washed dried, the resist on the non image area was removed and sealed in boiling water for 30 min. The image obtained on the anodised aluminium was sharp and clear.

EXAMPLE-5

Experiments as described in example 4 was repeated except for the colouring electrolyte which consists of cobalt acetate 60 g/l ammonium acetate 10 g/l and Boric acid 10 g/l. Counter electrode used was graphite. A brown colour was obtained at 0.3 A/dm^2 for 10 min. The image thus obtained after colouring was sharp and brown in colour.

The following are among the main advantages of the invention:

1. The image obtained by this process is light fast since inorganic pigments are depositedright at the bottom of the pores of the anodised aluminium.
2. This process eliminates the use of photosensitive chemicals such as silver salts to get black and white photographs.
3. All the materials needed for this process is indigenously available and are cheap.

Dated this 7th day of October, 1978

Sd/-

(I.M.S.MAMAK)
SCIENTIST ([redacted])
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

(Section – 10

AN ELECTROLYTIC PROCESS FOR THE PRODUCTION OF ANODISED ALUMINIUM PLATES WITH A DESIRED PATTERN IN COLOUR

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Rafi Marg, New Delhi - 110001, India, an Indian registered body incorporated under the registration of Societies Act (Act XXI of 1860)

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

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This is an invention by BALKUNJE ANANTHA SHENOI, Scientist and VENKATARAMAN BALASUBRAMANIAN, Senior Scientific Asstt. both of them are employed in Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India and are Indian Nationals.

This invention relates to an electrolytic process for the production of anodised aluminium plates with a desired pattern in colour thereon. The pattern may be in the form of labels, designs and photographs of light fast nature on anodised aluminium obtained without using silver by an electrolytic pigmentation process.

Hitherto it has been proposed to use methods such as silk method and offset printing techniques on anodised aluminium articles for making labels and designs. Silver deposited inside the pores of anodised aluminium was also used for preparing black and white photographs by adopting usual photographic technique.

There are some disadvantages in the above methods which are as follows:

Silk screen method can be used only for reproducing line composition, while fine lines and half-tones cannot be reproduced with great precision. In silk screen and offset methods the dyestuffs used for colouring are of organic nature and are not light fast and hence unsuitable for out door exposures. In the photographic method anodised aluminium is impregnated with photographic-method-are sensitive salts in the pores of the oxide film and developing the image, involves the use of costly chemicals such as silver salts.

The object of the present invention is to obviate the above disadgantages by using anodised aluminium (herein the word aluminium includes alloys of aluminium also) for making patterns like lables, designs and photographs by electrolytic pigmentation method using inorganic metal salt solution either using alternat-

-ing current or direct current.

The main advantages of the invention are:

1) The image obtained by this process is light fast since inorganic pigments are deposited right at the bottom of the pores of the anodised aluminium.

2) This process eliminates the use of costly photosensitive chemicals such as silver salt;

3) All the materials needed for this process is indigenously available andare cheap.

Accordingly this invention provides an electrolytic process for the production of anodised aluminium plates with a desired pattern in colour thereon which comprises applying a photosensative resist coating to an anodised surface of the aluminium plate, exposing same to photo positive transparency of the desired pattern, treating the exposed anodised plate to develop an image thereon, electrolytically colouring the imaged area of the plate using an inorganic metal salt solution in an electrolytic colouring bath, removing the photo-resist layer and sealing the pattern formed on the plate.

The process of the invention consists of anodising aluminium in 3 to 30% W/V sulphuric acid or oxalic acid or chromic acid or in a mixture of these acids using direct or alternating current of 0.3 A to 2.5 A/dm^2 at 20 $\pm$ 5°C for 20 to 40 minutes. The anodising voltage is either decreased or increased to the required value in the last five minutes of the anodising step to facilitate uniform colouring. Conventional acid resistant photo sensitive resist is uniformaly coated over the anodised surface and dried in the dark. The sensitised anodised aluminium plates is exposed to any film positive (half tone or line) using ultra violet radiation

for a period of 5 - 15 minutes. The exposed anodised plate is treated in a conventional developer. In this process unhardened portion of the resist will be removed by the developer. After developing the image, it is fixed and electrolytically coloured in a bath containing nickel, copper, cobalt, bismuth or tin salt solution either separately or in combination using as anode copper, nickel, graphite, tin or carbon employing alternative current. The anodised aluminium is made cathodic when direct current is employed. During electrolysis the image area is coloured. The colour depends upon the metallic salt solution, period of treatment and conditions of electrolysis. The image thus obtained is washed, dried and the resist on the surface is removed with the solvent. The photograph, design or bal label pattern thus obtained on anodised aluminium is sealed in boiling deionised or distilled water for 20 - 30 minutes. The pattern of the label, photograph or design thus obtain is elegant, smooth and colour fast. The patterns thus obtained are most suitable for outdoor architectural applications.

The following examples are given to illustrate the invention and not to limit the scope of the invention.

EXAMPLE I

Mechanically polished degreased 2S Aluminium plate of size 3" x 4" with 1" handle was first alkali cleaned in 10

sodium hydroxide solution for 2 minutes and wash in tap water and desmutted in 20% HNO_3 for 2 minutes. The aluminium plate thus cleaned was washed and rinsed with distilled water and jugged using aluminium jig. The plate was anodised using direct current in 10% V/V sulphuric acid electrolyte (sp.gr.1.84) at 20 ± 2°C for 30 minutes at 1.5 A/dm^2 current density. The anodised aluminium plate was washed and dried in the cold. Conventional acid resistant photo resist was applied on the surface uniformly using a coating device. The coated photo sensitive resist was allowed to cold dry in the dark. The sensitised anodised aluminium plate thus obtained was exposed to ultraviolet source through a photo positive for 10 minutes. The exposed plate was developed in trichloroethylene and washed in tap water and rinsed with distilled water. The anodised and sensitised plate was taken as one electrode and cooper as the other electrode, electrolytic colouring was carried out using alternating current at a current density of 0.4 A/dm^2 in an electrolyte containing 20 g/l copper sulphate with pH 1.5 adjusted with sulphuric acid. The plate was coloured for 5 minutes at 9V to get copper red colour. The plate was washed dried and the photo resist was removed with trichloroethylene and sealed in boiling distilled water for 30 minutes. The image obtained was very clear and sharp.

EXAMPLE-2

B51 S aluminium alloy plate was precleaned anodised and

sensitised with photoresist as given in example 1 and exposed to photo positive and the image was developed. Then the sensitised aluminium alloy plate was electrolytically coloured in a metal salt solution containing 20 g/l bismuth oxide, 2 g/l gelatin and 10 g/l sulphuric acid. The anodised aluminium plate was held as cathode using a graphite anode in the above electrolyte and 2.6 V direct current was passed for 20 minutes to get grey colour. The coloured image was washed, dried the photoresist was removed and sealed in boiling deionised water for 20 minutes. The image obtained was sharp and clear.

EXAMPLE -3

26S aluminium alloy plate was precleaned as in example 1 and anodised using D.C. in 10% W/V sulphuric acid electrolyte at 1.5 A/dm^2 current density for 25 minutes and later the anodising voltage was risen to 20V and further anodised for 5 more minutes . The anodised plate thus obtained was washed, rinsed, dried and coated with photosensitive resist and cold dried in the dark. The dried plate was exposed to ultraviolet radiation through a photopositive. The image was developed using trichloroethylene. The plate was washed, rinsed and electrolytically coloured using A.C. in a Nickel bath containing Nickel sulphate 100 g/l, Boric acid 50 g/l, ammonium sulphate 30 g/l and copper sulphate 10 g/l. The pH of the electrolyte was adjusted to 4 and electrolytic colouring was carried out using nickel as counter electrode. The electrolysis was carried out for 10 minutes at 0.4 A/dm^2

to get a brownish black colour. Later the photoresist on the non-image area was removed and sealed in boiling hot water. The image obtained was sharp and uniform.

EXAMPLE-4

578 aluminium alloy was polished precleaned as in example 1 and anodised in 20% V/V sulphuric acid containing 1%. Ferric ammonium sulphate using alternating current at 2.3 A/dm^2 current density for 30 minutes. The anodised plate was coated with photosensitive resist in the dark and dried well. The sensitised plate was exposed to ultraviolet through positive transparency for 10 minutes and the image developed. The developed plate was electrolytically coloured using A.C in a bath containing stannous sulphate (saturated) and 10 g/litre sulphuric acid using graphite as counter electrode. The image area of the anodised plate was coloured black in 10 minutes at 0.4 A/dm^2 current density. The coloured plate was washed dried, the resist on the non-image area was removed and scaled in boiling distilled water for 30 minutes. The image obtained on the anodised aluminium was sharp and clear.

EXAMPLE - 5

28 aluminium sheets was polished, cleaned anodised sensitised with photo resist and the image was developed as given in example 1. The image developed aluminium plate was electrolytically coloured using A.C in a colouring

electrolyte consisting of cobalt acetate 60 g/l, ammonium acetate 10 g/l and boric acid 10 g/l with graphite as counter electrode. A brown colour was obtained at 0.3 A/dm^2 for 10 minutes. The image thus obtained after colouring was sharp and clear.

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WE CLAIM :

1. An electrolytic process for the production of anodised aluminium plate with a desired pattern in colour thereon comprising applying a photosensative resist coating on to an anodised surface of the aluminium plate, exposing same to ~~the~~ photo positive transparency of the desired pattern, treating the exposed anodised plate to develop an image thereon, electrolytically colouring the imaged area of the plate using an inorganic metal salt solution in an electrolytic colouring bath, removing the photo-resist layer and sealing the pattern formed on the plate.

2. The process as claimed in claim 1 wherein the electrolytic colouring bath consists of metal salt solution of copper, nickel, cobalt, tin or bismuth either separately or in combination.

3. The process as claimed in claims 1 and 2 wherein the metal salt solution has concentration range of 1 to 10% W/V and a pH range of 1 to 5.5.

4. The process as claimed in any of the preceding claims wherein the anode used may comprise nickel, copper, tin, carbon or graphite the cathode being the anodised aluminium plate.

5. The process as claimed in any of the preceding claims wherein the current employed for electrolytic colouring is in the current density range of 0.3 A/dm^2 to 2.5 A/dm^2.

6. An electrolytic process for the production of anodised aluminium plate with a desired pattern in colour thereon substantially as herein described and illustrated in examples 1-5.

Dated this 10th day of October, 1979.

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